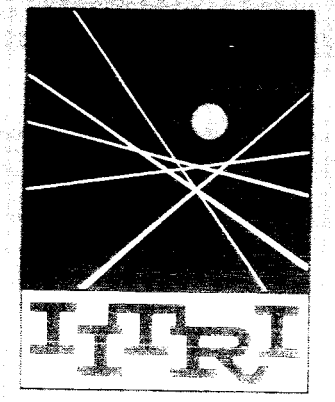

IIT RESEARCH INSTITUTE

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Technology Center Chicago, Illinois 60616

Report No. IITRI-C207-27
(Interim Report)

STABLE WHITE COATINGS

Jet Propulsion Laboratory
Pasadena, California

IIT RESEARCH INSTITUTE

(NASA CR-53086)

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STABLE WHITE COATINGS

July 15, 1963 to November 30, 1963

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FOREWORD

This is Report No. IITRI-C207-27 (Interim Report) of Project C207, Contract No. 950111 (subcontract under NASA Contract NAS7-100), entitled "Stable White Coatings." The report covers the period from July 15, 1963, to November 30, 1963. Previous Interim Reports, No. ARF-3207-5 and ARF-3207-14, and a Summary Report, No. IITRI-C207-25, were issued in April 1962, November 1962, and August 1963, respectively. This report is prepared for Mr. William F. Carroll, JPL Cognizant Engineer.

Major contributors to the program during this period included Gene A. Zerlaut (Project Leader); Y. Harada (inorganic coatings); Warren E. Jamison (space-chamber operation); Dr. Caroline D. Miller (attenuated total reflectance studies); O. Harry Olson (optical measurements); Richard G. Reichel (methyl silicone synthesis); and Douglas G. Vance (silicone paint preparations and optical measurements). Dr. Theodore H. Meltzer provided administrative supervision during this period. Contributions to this report were made by Dr. C. D. Miller and R. G. Reichel.

Data are recorded in Logbooks C13408, C13817, and C14177.

Respectfully submitted,

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ABSTRACT

STABLE WHITE COATINGS

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Investigations were continued in the development of white thermal-control coatings possessing good stability to ultraviolet irradiation in vacuum. This report describes studies aimed at the establishment of optimum manufacturing conditions for the three most promising paint systems. Of special importance were the formulation and synthesis parameters; storage, soiling, and cleaning experiments; room-temperature curing studies on the silicone paints; and zinc oxide bleaching experiments.

Aged silicate paints were less resistant to ultraviolet irradiation in vacuum than freshly prepared specimens. Also, zinc oxide was shown to be clearly superior to both tin oxide and calcined china clay, which showed promise in earlier tests. Diethylenetriamine produced room-temperature cure of the methyl silicone paints but caused adverse physical effects as well as ultraviolet degradation in anything but small quantities. Zinc oxide paints were found to exhibit no more than 1% reflectance increases (bleach) on admission of air to irradiated specimens. Recent studies with attenuated total reflectance have eliminated some of the earlier difficulties experienced in applying this technique. It now appears that attenuated total reflectance could be a useful tool in the assessment of damage due to ultraviolet irradiation in vacuum.

AUTHOR

GLOSSARY

ATR	Attenuated total reflectance.
α	Solar absorptance.
α_1 and α_2	$\alpha_1 + \alpha_2 = \alpha$. α_1 corresponds to that half of the sun's energy below 7000 A, and α_2 corresponds to that half above 7000 A.
$\Delta\alpha$	Change in absorptance.
ε	Emittance
α/ε	Ratio of solar absorptance to infrared emittance.
ESH	Equivalent sun-hours of extraterrestrial ultraviolet radiation.
Me/Si	Molar ratio of methyl groups to silicon atoms.
PBR	Pigment/binder ratio.
PVC	Pigment volume concentration.

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STABLE WHITE COATINGS

I. INTRODUCTION

The principal objective of this program was the development of a white spacecraft thermal-control coating with exceptional stability to extraterrestrial solar radiation. Therefore the primary requirements were that:

- -the coating have a high resistance to ultraviolet radiation in vacuum, namely, the change in the ratio of solar absorptance to infrared emittance be only 10% after 1 year of exposure
- -the ratio of solar absorptance to infrared emittance of the coating be 0.30 or less
- -the infrared emittance of the coating be approximately 0.9.

The other requirements were that:

- -the coating cure at 300°F or less
- -the coating remain adherent to aluminum alloys and other spacecraft structural materials through temperature changes of 50°F per minute between 200 and -100°F.

During the course of this program it soon became evident that the first requirement was unusually severe, namely, that the change in the ratio of solar absorptance to emittance be only 10% after 1 year (equivalent) of exposure.

However, these investigations resulted in the development of three satisfactory paint systems; two of these systems changed only about 0.01 in solar absorptance after an exposure to over 4000 equivalent sun-hours (ESH). These two coatings were formulated by using a high-purity zinc oxide, SP 500, in conjunction with either a methyl silicone polymer synthesized in our laboratories or a commercial potassium silicate, PS7; these coatings are designated S-33 and Z93, respectively (Summary Report No. IITRI-C207-25). The third coating, S-13, was also pigmented with SP 500 zinc oxide and was based upon General Electric's LTV-602 methyl silicone elastomer (IITRI's experimental methyl silicone is a resin). S-13 is a highly flexible, elastomeric coating, which can be prepared in free, detached sheets and subsequently used as a decal, or "wallpaper," type of thermal-control coating. S-13 exhibited an increase in solar absorptance of 0.06, or about 30%, compared

to about 10% for Z93 and S-33 after 4200 ESH (nearly 1/2 year of simulated space environment).

Soiling and cleaning tests were conducted on both the silicate and the experimental silicone paints; shelf life, storage, and aging tests were conducted on the inorganic silicate system. These tests were performed in an effort to ascertain the various problems which occur during the field application of these thermal-control coatings. Additional experimental methyl silicone resins were prepared in a continued effort to establish the process parameters for the pilot manufacture of the materials.

Studies were again initiated on the use of attenuated total reflectance (ATR) as a technique to assess the damage to paint media on exposure to ultraviolet in vacuum. It is hoped that this analytical tool will facilitate the observation of ultraviolet-induced changes in the chemical structure of potentially useful inorganic and polymeric paint media.

Finally, the recovery, or bleaching reaction, of discolored paints was more carefully investigated. This bleaching reaction has been found to be a problem only in the evaluation of severely degradable systems. Bleaching of zinc oxide-pigmented methyl silicone and potassium silicate coatings has not been observed in the day-to-day measurements.[1] The general practice in making these measurements has been to maintain the irradiated specimens in the dark until their reflectance has been measured. Since bleaching occurs in the vicinity of 4400 A, the visible reflectance was measured first and was always completed within an hour after the specimen had been removed from the simulation chamber. However, because of the importance of assuring that the relatively stable zinc oxide coatings do not exhibit significant bleaching reaction in the interim between removal from the simulation chamber and reflectance measurement, a rather careful experiment was designed to determine the amount of bleaching, if any, which might be expected to occur in zinc oxide systems.

The techniques used to measure the solar absorptance before and after exposure as well as a description of the ion-pumped solar simulation chamber are given in the Summary Report.[1]

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[1] Zerlaut, Gene A., and Harada, Y., "Stable White Coatings," Report No. IITRI-C207-25 (Summary Report), August 27, 1963.

II. POTASSIUM SILICATE PAINTS

A. Effects of Controlled Storage, Soiling, and Cleaning

Several space-simulation experiments were conducted to study the factors which affect the stability of the inorganic silicate coatings. The histories of the various samples are given in Table 1,and the results of ultraviolet irradiation on these specimens are given in Table 2.

Previous experiments had shown the beneficial effects of a 500°C heat treatment on the stability of coatings. As seen in Table 1, this effect was manifested for the shelf-life composition, Z98; an earlier test had shown a $\Delta\alpha$ of 0.073 after 1780 ESH. However, the degradation of the sample cured in a carbon dioxide atmosphere was not significantly affected by heating to 500°C. There is a possibility, then, that the degradable component in the shelf-life sample is zinc carbonate, a material which begins to lose carbon dioxide at 300°C. The degradable component in the carbon dioxide-cured sample could be potassium carbonate, which does not decompose until it reaches a temperature of 800°C. This hypothesis will be investigated by differential thermal analysis and gas-train analysis for carbon dioxide content.

Application of a second zinc oxide-silicate coating on a cured coating is difficult because the porous undercoating absorbs the liquid so rapidly that a friable powdery surface results. However, a rapid, heavy spray of a second coating does yield a satisfactory surface. Of the three samples which received a second coating, Z101 was the most amenable to this topcoat, because the pores were partially closed. Surprisingly, this same sample underwent the smallest reflectance loss; an earlier test indicated that coating an uncleaned subcoat was not sufficient to retain stability. Further experiments will be conducted to study this anomaly. Nevertheless, the present results suggest the feasibility of applying a topcoat over a soiled area.

The 2120-ESH tests revealed moderate degradation for samples which had been protectively stored for 8 months. In a previous experiment, for 1650 ESH, samples with identical processing but stored for only a month exhibited $\Delta\alpha$'s of 0.018 (desiccator) and 0.014 (Saran). Wrapping in Saran for long periods of time does not appear adequate to retain stability. There is a possibility that a loss in stability could occur through a mechanism, perhaps inherent in a zinc oxide-silicate system, not influenced by atmospheric conditions.

Table 1

SPECIMEN HISTORIES FOR STORAGE,
SOILING, AND CLEANING EXPERIMENTS

Sample	History
Z97	Protected atmospheric storage, 4 months*.
Z98	Shelf-life sample. Formulation originally prepared and milled 4 months prior to remilling and application. Coating heated at 500°C for 2 hr.
Z99	Cured in carbon dioxide atmosphere. Heated at 500°C for 2 hr.
Z100	Original coating soiled with dirt, cleaned with detergent and water, then coated with 4-mil topcoat.
Z101	Original coating soiled with dirt, then coated with 4-1/2-mil topcoat. No attempt made to clean initial coating.
Z102	Original coating soiled with vacuum oil, cleaned with detergent and water, then coated with 5-mil topcoat.
Z103	Cured in a desiccator over Ascarite and Drierite for 22 hours and stored under Saran Wrap for 8 months.
Z104	Cured and stored in the desiccator for 8 months.
Z105	Storage, four weeks*.
Z106	Storage, six weeks*.
Z107	Storage, six weeks*.
Z108	Storage, six weeks*.
Z109	Storage, two weeks*.
Z110	Storage, four weeks*.
Z111	Storage, seven weeks*.
Z112	Storage, four weeks*.
Z113	Storage, four weeks*.

*Stored between sheets of vellum.

Table 2

EFFECT OF UV IRRADIATION IN VACUUM
ON OPTICAL PROPERTIES OF INORGANIC SILICATE PAINTS

Sample	Composition: Pigment	Composition: Pigment Calcination	Composition: PBR	Composition: % Solids Content	Exposure: ESH	Exposure: Solar Factor	Solar Absorptance: α_1	Solar Absorptance: α_2	Solar Absorptance: α	Solar Absorptance: $\Delta\alpha$
Z97	SP 500	16 hr at 700°C	4.3	56.9	0		.095	.061	.156	
	ZnO				730	8.4	.112	.060	.171	.015
Z98	SP 500		4.3	46.3	0		.088	.049	.137	
	ZnO				730	8.4	.105	.051	.156	.019
Z99	SP 500	16 hr at 700°C	4.3	56.9	0		.101	.072	.174	
	ZnO				730	8.4	.170	.082	.252	.078
Z100	SP 500	16 hr at 700°C	4.3	56.9	0		.096	.054	.149	
	ZnO				730	8.4	.110	.055	.165	.016
Z101	SP 500	16 hr at 700°C	4.3	56.9	0		.091	.055	.146	
	ZnO				730	8.4	.102	.053	.155	.009
Z102	SP 500	16 hr at 700°C	4.3	56.9	0		.091	.056	.147	
	ZnO				730	8.4	.109	.054	.163	.016
Z103	SP 500	16 hr at 700°C	4.3	56.9	0		.096	.064	.160	
	ZnO				2120	10.2	.132	.064	.196	.036
Z104	SP 500	16 hr at 700°C	4.3	56.9	0		.090	.064	.153	
	ZnO				2120	10.2	.114	.067	.181	.028
Z105	55-LO	16 hr at 700°C	4.3	61.7	0		.098	.068	.166	
	ZnO				2070	10.8	.114	.069	.183	.017
Z106	SP 500	16 hr at 700°C	4.59	56.7	0		.093	.070	.163	
	ZnO	Kasil 1			1700	9.2	.108	.069	.177	.014
Z107	SP 500	16 hr at 700°C	4.59	56.7	0		.091	.069	.160	
	ZnO	Kasil 88			1700	9.2	.115	.067	.182	.022
Z108	SP 500	16 hr at 700°C	2.13	55.9	0		.125	.145	.270	
	SnO				1700	9.2	.144	.132	.276	.006
Z109	C.P.		4.3	64.4	0		.062	.109	.171	
	ZrO_2				2120	10.2	.141	.100	.242	.071
Z110	C.P.		4.3	64.4	0		.067	.112	.179	
	ZrO_2				2070	10.8	.158	.117	.274	.095
Z111	C.P.		4.3	64.4	0		.064	.110	.173	
	ZrO_2				1700	9.2	.139	.115	.253	.080
Z112	C.P.		4.3	61.7	0		.112	.155	.267	
	SnO_2				2070	10.8	.196	.160	.357	.090
Z113	Molochite		4.3	61.7	0		.121	.124	.245	
	No. 6*				2070	10.8	.183	.130	.313	.068

*Calcined china clay

The superior stability of zinc oxide over tin oxide and calcined china clay was clearly shown in the 2070-ESH test. The small $\Delta\alpha$ exhibited by the 55-LO (Z105) sample suggests a reevaluation of this material.

Philadelphia Quartz Company has advised that their analyses have shown that both Kasil 88 and Kasil 1 compare in purity to PS7. The Kasils are lower in alkalinity; they have alkali-to-silica mole ratios of 1:3.45 and 1:3.92, and PS7 has a ratio of 1:3.31. Preparation of Kasil-bonded coatings resulted in slight improvement of surface hardness.

Exposure of the Kasil samples in the 1700-ESH test resulted in significant crazing of these coatings. The brittleness of the higher-silica vehicles would limit their use despite the comparable (to PS7) stability shown by these systems.

Surprising stability was displayed by the low-PBR composition. The small $\Delta\alpha$ was due in larger measure to the bleaching in the infrared as shown by α_2. Earlier experiments have shown that pigments do not reveal a reflectance increase in the infrared after irradiation, whereas paints do. The even stronger crossover effect, i.e., the intersection of the spectral reflectance curves before and after exposure for sample Z108 at a wavelength of about 10,000 A, demonstrates that potassium silicate is responsible for this phenomenon. Furthermore, $\Delta\alpha_1$ for this sample was not excessive. Thus a closer perusal of high-binder systems to exploit both the α_2 improvement and improved physical properties is in order.

A zirconia paint was included in each of the tests as a control. Although no direct relationship between $\Delta\alpha$ and ESH was observed, the degradation was similar for all samples. A ZrO_2 sample will also be included in future tests; with more tests, it is anticipated that a clearer indication of the validity of the space simulation will be seen.

An investigation of the effect of storage of zinc oxide-silicate coatings in a variety of plastics has been initiated. The materials which are being used are Tedlar, Teflon type A, Lexan, H-polymer, and Mylar. Samples are stored in intimate contact with these plastics under air and also in an inert helium atmosphere. The effect of humidity is also being studied. Two sets of samples are being stored in a 100% humidity room; one set was introduced into this atmosphere immediately after the paint was applied, and the second after drying in air for 6 days.

B. Effect of Formulation Parameters on Physical Properties

Experiments with the standard formulation, SP 500 zinc oxide calcined at 700°C for 16 hr plus PS7 potassium silicate at a PBR of 4.30, have shown that the solids content can be increased to 59.8% without impairing sprayability. This decrease in diluent seems to result in a tougher coating. The use of SP 500 calcined at 700°C for 112 hr makes spraying difficult; the coarser particles produced by this extended calcination prevent good atomization.

C. Fluorescence and Pigment Degradation

Studies have been initiated to determine the effects of space simulation on the fluorescence of materials and also to assess the utility of this optical phenomenon. A variety of paints and pigments, both irradiated during space simulation and unirradiated, were examined under ultraviolet light. A Hanovia mercury-arc quartz lamp, fitted with a filter which permits passage of wavelengths from 320 to 390 mμ, was used.

Preliminary visual observation revealed that the discolored surfaces of various pigments subjected to ultraviolet irradiation in vacuum in the early screening tests fluoresced a variety of colors to various degrees. Scratching of these surfaces to reveal the material below showed little or no fluorescence of the original materials. Among the powders which exhibited these properties were zirconia, zircon, talc, kaolin, alumina, metaphosphates of aluminum and potassium, calcium carbonate, calcium fluoride, calcium silicate, and barium carbonate.

Paradoxically, irradiated SP 500 samples showed the opposite behavior, i.e., a decrease in fluorescence. Both samples B and C (Table 3) underwent this loss, although the material below the exposed surface showed the characteristic natural fluorescence of zinc oxide. The fluorescence of zinc oxide is thought to be caused by the presence of interstitial zinc atoms or other crystal imperfections. The results suggest that exposure of zinc oxide powder to simulated space effects a stabilization or approach of stoichiometry.

Zinc oxide-potassium silicate paints did not undergo a similar change in fluorescence upon irradiation. Furthermore, the scratched undersurface showed little or no emission. Another treatment which affects fluorescence is heating. Paints heated at 140°C exhibited less fluorescence, and when these paints were heated at 500°C, the fluorescence decreased even more.

Some materials were black under ultraviolet light (i.e., they did not fluoresce). Silicate paints of tin oxide, china clay, and zirconia fall in this category.

The preliminary investigations of fluorescence of materials suggests a complementary tool for analysis of degradation in a space environment. Determinations of the intensity and the wavelength of the emitted light are necessary to define fluorescence. A phosphorimeter will be used in some future experiments; adaptation of the Cary spectrophotometer will also be attempted.

D. Doping Zinc Oxide with Trivalent Atoms

Weyl[2] has reported that sintering of zinc oxide is inhibited by the use of a small amount of trivalent atoms such as aluminum and gallium, which decrease oxygen vacancies in the crystals. Such a phenomenon could enhance the stability of zinc oxide. On the basis of Weyl's work, 1 mol % alumina as an aqueous nitrate was mixed with zinc oxide. The mixture was evaporated to dryness and calcined at 300°C to decompose the nitrate to the oxide. The resulting sample (A) was prepared as a compacted powder. SP 500 zinc oxides calcined at 700°C for 16 hr (sample B) and for 112 hr (sample C) were also included in this experiment as pigment samples. Two disks of AZO-77 zinc oxide (99.80% purity, 0.14-mμ particle size), pressed at 5000 psi (sample D) and 10,000 psi (sample E), were fired at 700°C and also exposed in this test for 960 ESH.

The results, tabulated in Table 3, reveal that the small amount of added alumina was detrimental to stability. Discoloration was not continuous; a mottled appearance suggested degradation of segregated particles of alumina. The $\Delta\alpha$'s of the various zinc oxides are too small to show any significant trends due to calcination times or density differences.

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[2] Weyl, W. A., "Atomistic Interpretation of the Mechanism of Solid State Reactions and of Sintering," Ceramic Age, 60, 5, 28 (1952).

Table 3

EFFECT OF 960 ESH OF UV RADIATION IN VACUUM
ON OPTICAL PROPERTIES OF ZINC OXIDES RECEIVING VARIOUS TREATMENTS
(Solar Factor = 8.9)

Sample	Exposure, ESH	Solar Absorptance α_1	α_2	α	$\Delta\alpha$
A	0	.093	.046	.139	
	960	.175	.056	.231	.092
B	0	.091	.037	.128	
	960	.092	.041	.134	.006
C	0	.096	.037	.133	
	960	.096	.037	.133	.000
D	0	.205	.099	.304	
	960	.210	.098	.308	.004
E	0	.208	.105	.313	
	960	.207	.104	.311	-.002

III. ZINC OXIDE-PIGMENTED METHYL SILICONE PAINTS

A. Paint Formulation

The formulation data for all the silicone paints are given in Table 4. Pigment/binder ratios are shown as both weight and volume ratios. Weight ratios are designated PBR (pigment/binder ratio) and volume ratios are designated PVC (pigment volume concentration). In the table, use of the tetrabutoxy titanium curing agent is denoted by TBT. Similarly, the diethylenetriamine catalyst is denoted by DETA. SP 500 zinc oxide can be obtained from the New Jersey Zinc Company, and the LTV-602 polymer and SR-17 resin can be obtained from the Silicone Products Department of General Electric.

S-13 was cured at room temperature for 16 hr, and S-34 and S-37 were cured at room temperature for 2 hr. Coatings S-35 and S-39 were cured at 500°F for 1 hr, and coatings S-36 and S-40 were cured at room temperature for 4 days. S-38 received the following cure schedule: 6 min at 250°F, 6 min at 400°F, and 10 min at 500°F.

Table 4

FORMULATION DATA FOR SILICONE PAINTS

Paint No.	Ingredients, parts by wt.		PVC, %	PBR	Solids % by vol.
S-13	SP 500 zinc oxide	240.0	30	2.40	40
	LTV-602 polymer	100.0			
	SRC-05 catalyst	0.5			
	Toluene	183.8			
S-34	SP 500 zinc oxide	240.0	30	2.40	40
	LTV-602 polymer	100.0			
	DETA catalyst	>>1.0			
	Toluene	183.8			
S-35	SP 500 zinc oxide	269.0	35	2.69	35
	R-10 exptl. resin	100.0			
	TBT curing agent	1.0			
	Toluene	219.0			
S-36	SP 500 zinc oxide	269.0	35	2.69	35
	R-10 exptl. resin	100.0			
	DETA catalyst	1.0			
	Toluene	219.0			
S-37	SP 500 zinc oxide	240.0	30	2.40	40
	LTV-602 polymer	100.0			
	DETA catalyst	1.0			
	Toluene	183.8			
S-38	SP 500 zinc oxide	98.5	30	1.99	35
	SR-17 resin	100.0			
	Toluene	51.1			
S-39	SP 500 zinc oxide	269.0	35	2.69	35
	R-11 exptl. resin	100.0			
	TBT curing agent	1.0			
	Toluene	217.0			
S-40	SP 500 zinc oxide	269.0	35	2.69	35
	R-11 exptl. resin	100.0			
	DETA catalyst	1.0			
	Toluene	217.0			

B. Methyl Silicone Synthesis

Two molecularly distilled methyl silicone experimental resins were synthesized in further attempts to determine optimum pilot-manufacturing conditions. These resins are designated R-10 and R-11. The synthetic procedures are given below.

Experimental Resin R-10

A mixture of 154.8 g (1.2 mole) of dimethyldichlorosilane, 288 g (1.92 mole) of methyltrichlorosilane, and 900 g of anhydrous ether was added dropwise, over a period of 120 min, to an agitated ice bath. The ether layer was separated and washed with distilled water. This layer was then washed with a 5% solution of $NaHCO_3$, followed by three washings with distilled water. The ether solution was dried overnight over Drierite and was then evaporated at reduced pressure, leaving 209 g of colorless resin. The resultant resin was charged to an ASCO '50' Rota-Film molecular still and was distilled at an average temperature of 120°C and 0.02 mm Hg pressure over a 3.75-hr interval, yielding 84.8 and 88.6 g of high-boiling and low-boiling resin, respectively. The molecular weight of the higher-boiling fraction was 1700. The specific gravity was 1.120. Chemical analysis yielded 22.04% C, 6.39% H, 36.53% Si, and 36.14% O by difference.

A weight check of the glassware used in the above experiment indicated that 15.3 g of product adhered to the glass surface. It is also probable that additional silicone resin was lost in the water/ether separation, since ether is somewhat soluble in water.

Experimental Resin R-11

A mixture of 154.8 (1.2 mole) of dimethyldichlorosilane, 288 g (1.92 mole) of methyltrichlorosilane, and 400 g of anhydrous ether was added dropwise, over a period of 70 min, to an agitated ice bath. The ether layer was separated and washed with distilled water. This layer was then washed with a 5% solution of $NaHCO_3$, followed by three washings with distilled water. The ether solution was dried overnight over Drierite and was then evaporated at reduced pressure, leaving 195 g of colorless resin. The resultant resin was charged to the ASCO '50' Rota-Film molecular still and was distilled at an average temperature of 135°C and 0.18 mm Hg pressure over a 3.75-hr interval, yielding 123.6 g of high-boiling resin. The molecular weight was 1590. The specific gravity was 1.120. Chemical analysis yielded 23.20% C, 6.14% H, 36.10% Si, and 34.56% O by difference.

Molecular weights were determined on a Mechrolab vapor-pressure osmometer, which operates on the principle of vapor-pressure lowering of a solvent solution. A drop of solvent and a drop of solution are suspended side by side in a closed chamber that is saturated with solvent vapor. The difference in vapor pressure between the two drops causes a differential mass transfer between the drops and the solvent vapor phase, which results in lower evaporation from the solution drop. The mass transfer causes a temperature difference between the drops (heat of vaporization). This difference is proportional to the vapor pressure lowering and thus to the solvent concentration.

Polymer molecules have a strong tendency to show concentration dependency in these measurements. Therefore a concentration series was made for samples of resin R-10, which is considered to be a better separation product.

R-10 Concentration	Molecular Weight
0.1586 g/10 ml	1482
0.3187	1675
0.4759	1700
0.7931	1705

These results show the concentration dependency and indicate that future measurements should be made in the concentration range of 0.5 to 0.6 g/10 ml.

C. Curing Experiments and Physical Properties

1. Use of DETA with LTV-602

Diethylenetriamine (DETA) was added in small increments to the elastomeric LTV-602 silicone polymer. The results of this experiment are given in Table 5.

2. Physical Properties of Experimental Resins

Experimental resins R-10 and R-11 differed markedly in physical properties from previous distilled resins R-5A, R-8, and R-9 (Report No. IITRI-C207-25, Summary Report). R-10 and R-11 are of considerably lower molecular weight than R-5A, R-8, and R-9. Although we have insufficient data to determine the optimum pilot-manufacturing conditions during resin synthesis, some trends are indicated by the compilation of data obtained to date; these are presented in Table 6.

Table 5

DETA-CURED LTV-602

Amount		Remarks
DETA	LTV-602	
1 drop	20 g	Did not set in 30 min at room temperature. Cured in 10 min at 340°F. Gel still tacky. 15 min more at 340°F discolored material.
1 drop	10 g	Nearly set in 15 min at room temperature. 3 min at 340°F gave a full set. nonsticky. 15 min additional at 340°F discolored material.
2 drops	10 g	Full set in 1 hr at room temperature. Clear, nontacky.
3 drops	10 g	Full set in 3/4 hr at room temperature. Mass slightly cloudy and tacky.
4 drops	10 g	Full set in 3/4 hr at room temperature. Mass cloudy and quite tacky.
5 drops	10 g	Full set in 3/4 hr at room temperature. Mass very cloudy and very tacky.

Table 6

CONDITIONS DURING MOLECULAR DISTILLATION
OF EXPERIMENTAL RESINS

Resin No.	Distillation Temperature, °C	Pressure, mm Hg	Molecular Weight
R-5A	150	0.04	2290
R-8	108	0.04	2100
R-9	100	0.004	2000
R-10	120	0.02	1700
R-11	135	0.18	1590

Unlike the earlier experimental resins, R-10 and R-11 exhibited poor physical properties when heated to 500°F and cooled. Both resins when cured with TBT were nearly cured in 3 hr at 300°F (they were nontacky and firm) but required heating for 1 hr to 500°F to reach optimum hardness. All films cured with TBT and heated to 500°F cracked severely on cooling -- even when pigmented with SP 500 zinc oxide. Both resins when cured with DETA dried to the touch in 16 hr at room temperature and developed full hardness in 4 days (they were always nonglossy compared to TBT-cured specimens). Resins R-10 and R-11 fully cured in 1/2 hr at 150°F but cracked and fell off on cooling.

All DETA-cured pigmented specimens failed on the first immersion in liquid nitrogen. All TBT-cured pigmented specimens passed 10 cycles of immersion in liquid nitrogen followed by quick heating to 200°F. Coating S-36 failed when it was bent 30°; the whole film popped off. Coating S-39 cracked along the axis of the bend when bent 45°.

D. Stability to a Simulated Space Environment

The results of exposure of various methyl silicone paints to ultraviolet radiation in vacuum are given in Table 7.

The necessity for cleaning white thermal-control surfaces before simulation -- and, therefore, immediately before spacecraft lauching -- is evident from the degradation exhibited by the uncleaned specimen of S-13 irradiated for 2120 ESH.

Examination of Table 7 also shows that DETA catalyst can seriously affect the stability of methyl silicone paints, particularly if used in large quantity as in S-34. The $\Delta\alpha$ of 0.32 represents nearly a 100% increase in solar absorptance. Furthermore, the DETA-cured LTV-602 paint S-37 showed rather severe degradation even though only 1% catalyst was added based on polymer solids. The DETA-cured experimental methyl silicone resin paints (S-36 and S-40) did not exhibit as severe degradation as the DETA-cured LTV-602 elastomer paint S-37. Although paint S-36 cracked and chipped during space simulation, it was possible to compute the $\Delta\alpha_1$ (based upon visible reflectance) by reducing the aperture during measurement. The $\Delta\alpha_1$ of only 0.004 indicates the general level of stability which can be expected for these paints.

The paints cured with TBT and based upon experimental resins R-10 and R-11 showed exceptional stability in these tests. The solar absorptance of S-35 increased by only 0.008 in 2120 ESH of ultraviolet radiation in vacuum. S-37 exhibited similar resistance to space simulation. Of real significance

Table 7

EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF ZINC OXIDE-PIGMENTED METHYL SILICONE PAINTS

Paint No.	Remarks	Exposure ESH	Exposure Solar Factor	Solar Absorptance α_1	α_2	α	$\Delta\alpha$
S-13	5-gal batch	0		.101	.114	.215	
		2070	10.8	.134	.137	.272	.057
S-13	More than 10 wks old; uncleaned	0		.100	.080	.180	
		2120	10.2	.175	.108	.282	.102
S-34	xs DETA catalyst basic S-13 paint	0		.086	.089	.175	
		2070	10.8	.271	.217	.488	.313
S-37	1% DETA; basic S-13 paint	0				.183	
		1700	9.2			.247	.064
S-35	R-10 resin + TBT (1%)	0		.120	.106	.226	
		2120	10.2	.127	.107	.234	.008
S-36	R-10 resin + DETA (1%)	0		.117	.103	.220	
		2120	10.2	.121*	Cracked off		(.004)
S-39	R-11 resin + TBT (1%)	0				.231	
		1700	9.2			.238	.007
S-40	R-11 resin + DETA (1%)	0				.198	
		1700	9.2			.219	.021
S-38	GE's SR-17 resin	0				.247	
		1700	9.2			.453	.206

*S-36 cracked and partially fell off and only the visible could be measured with constructed aperture.

is the fact that coating S-35 was soiled with grease metal shavings and general machine shop dirt. It was subsequently cleaned with Alconox (5%) and distilled water.

Like the SR-80 resin (IITRI-C207-25, Summary Report), General Electric's SR-17 silicone resin was also reported to be a wholly methyl resin. Also like SR-80, a paint based on SR-17, paint S-38, showed a structure slightly different from pure methyl resins on infrared analysis, and similar to SR-17 paints, S-38 severely degraded on ultraviolet irradiation in vacuum. Although the exact constituents of these resins have not been determined, they do not possess phenyl constituents. More careful correlations between infrared spectra (i.e., structure), ultraviolet transmittance spectra, and stability in an ultraviolet/vacuum environment are being made.

IV. ZINC OXIDE BLEACHING EXPERIMENT

This test was an investigation of possible bleaching of the zinc oxide-silicate system on removal from a vacuum. A chamber which permits measurement of the visible spectrum reflectance of a sample under vacuum was designed and constructed. The apparatus (Figure 1) could be valved off from the ion pump and attached to a reflectometer. A vacuum ionization gage attached directly to the system showed a pressure increase from 10^{-7} to 10^{-4} torr on removal from the pump; at this point equilibrium appeared to be attained.

The sample used was S-25, an SP 500 zinc oxide-pigmented experimental silicone resin (Summary Report IITRI-C207-25). It was exposed to 837 ESH at a solar factor of 8.8. Visible reflectance curves were obtained for the unirradiated sample in the test chamber under vacuum and also after admission of air. The reflectance under vacuum was 0.5 to 1% higher than that in air. This difference might be attributable to a slight adjustment of the system in relation to the reflectometer due to relaxation of the O-ring upon release of the vacuum. Figure 2 contains these curves as well as those obtained after space simulation.

Similar measurements made after completion of irradiation did not reveal the slight difference in reflectance; admission of air resulted in a curve identical to that under vacuum. Thus slight bleaching might have occurred. Coincidence of the curves remained static on remeasuring after 15, 30, 120, 180, and 360 min.

Solar spectral reflectance was determined on the sample in the usual manner, i.e., before it was in the apparatus and before and after exposure; the $\Delta\alpha$ was 0.003. If 1% bleaching occurred throughout the spectrum, including the infrared portion, the $\Delta\alpha$ would be 0.012. The important point is that even if the biggest shift in reflectance occurred, as suggested by the experiment, the change in solar absorptance due to simulation is limited.

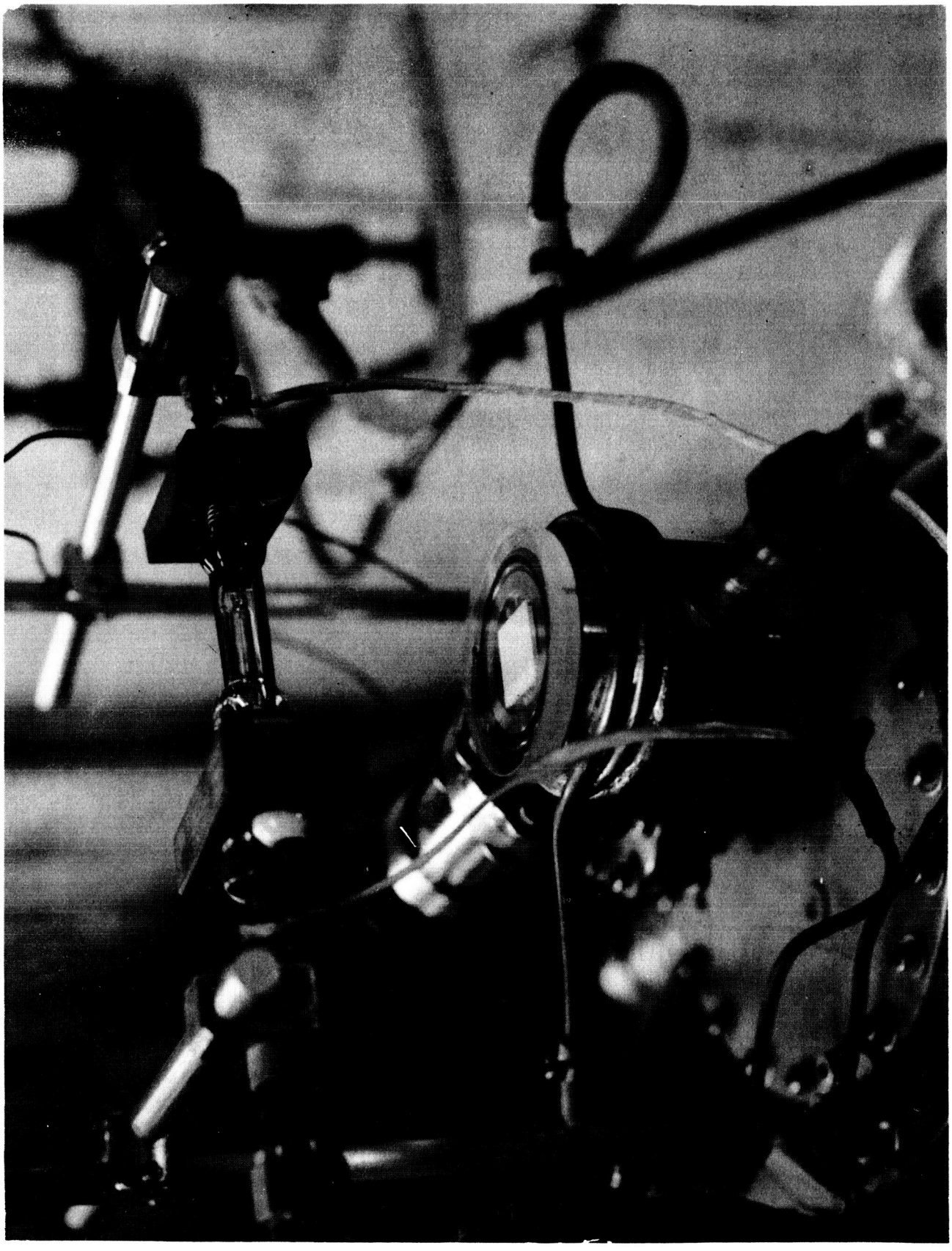

Figure 1 SINGLE SAMPLE UV/VACUUM CHAMBER FOR ZINC OXIDE BLEACHING EXPERIMENTS

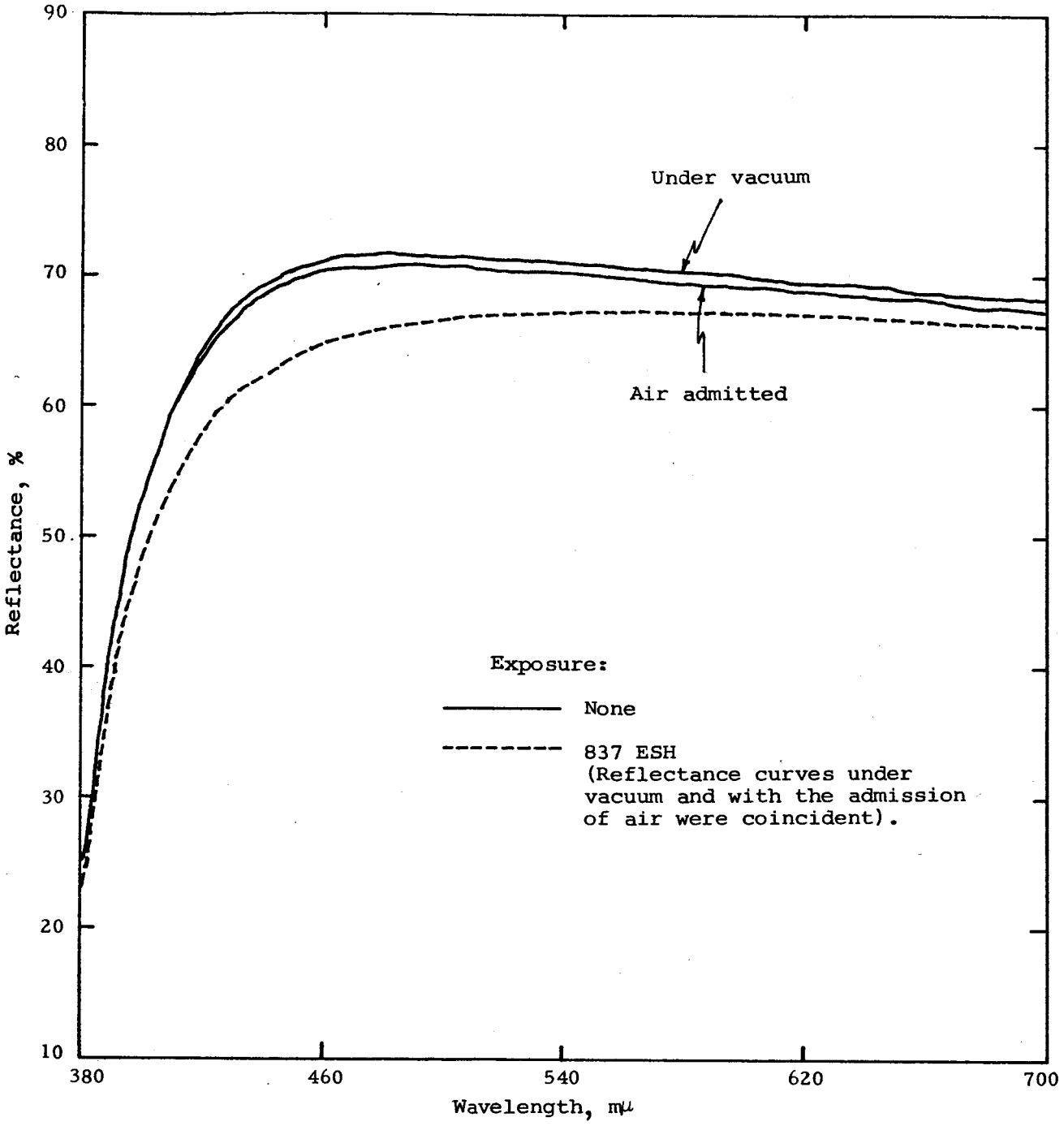

Figure 2

REFLECTANCE CHANGES OF ZINC OXIDE-SILICONE COATING DUE TO UV IRRADIATION IN VACUUM

V. ATTENUATED TOTAL REFLECTANCE STUDIES

The use of attenuated total reflectance spectroscopy to characterize polymer surfaces is attractive in principle, but previous efforts to make this a workable tool have not been particularly successful. The most troublesome difficulty was the lack of reproducibility. When small alterations in surface composition are being sought, it is obviously necessary that small differences in the spectra be significant.

In some of our earliest work we observed the appearance of "trans unsaturation" absorption after photolysis. This phenomenon proved unreproducible and was apparently spurious. A further difficulty was deterioration of the physical condition of the surfaces upon photolysis. At first it seemed that the problem was a lack of contact between the polymer surface and the face of the prism. Good optical contact is difficult to obtain when the surface of interest is seriously eroded. Even the use of a wetting agent such as Nujol is almost useless when the surface is spongy.

However, attempts to evaporate thin films of the prism material onto the polymer surface led to poorer, not better, spectra. On the basis of these results, it is tentatively suggested that the silver chloride film was partially photodecomposed by the light in the room to give a metallic reflection at the interface, thus reducing the change in the reflection in the region of an absorption band.

It seemed that fairly good spectra could be obtained at certain wavelengths but not at others. This suggested that the refractive indices of the polymer and the prism material were suitable only in a limited wavelength region, and other prism materials with different indices of refraction were investigated. (The refractive index of the polymer must be lower in order for total reflection to occur. In the region of an absorption band, where the refractive index becomes anomalous, this condition is no longer fulfilled and total reflectance is no longer obtained.)

In recent work a new series of spectra were obtained with silver chloride, the usual prism material, at various angles of incidence, and other series were obtained with sodium chloride and KRS-5 as the prism materials. The results are shown in the accompanying figures, which show the transmission spectrum of a typical polycarbonate (Figure 3, chosen for convenience and good spectral detail) and the ATR spectra of the same polymer against silver chloride, sodium chloride, and KRS-5 at various angles of incidence (Figures 4 through 7).

Sodium chloride gives excellent spectra in the region below 4.5 μ. Above this wavelength, refractive index inversion obviously occurs, as indicated by the low total reflectance. However,

sodium chloride is extremely brittle, and it is difficult to exert sufficient clamping force to ensure reproducible contact without cracking the prism.

KRS-5, having a much higher refractive index, gives recognizable spectra throughout the entire 2- to 15-μ region, although the optimum angle of incidence changes from about 42 to 50° at the longer wavelengths. The intensity of the bands is markedly sensitive to small differences in the angle of incidence, differences which may not be reproducible in the relatively crude apparatus available. KRS-5 also has the advantages of being more stable than silver chloride and more durable than sodium chloride.

Silver chloride is useful to about 8 μ at very high angles of incidence, as one might predict from consideration of the refractive indices of these three optical materials.

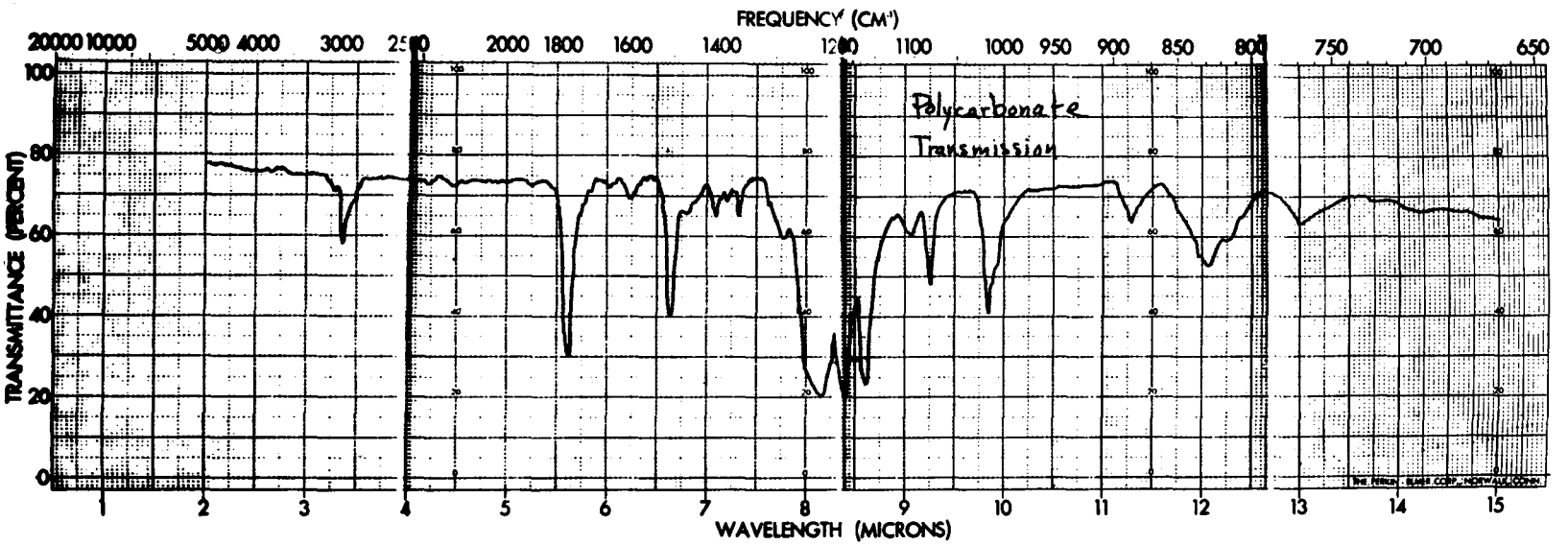

Figure 3

TRANSMISSION SPECTRUM OF POLYCARBONATE

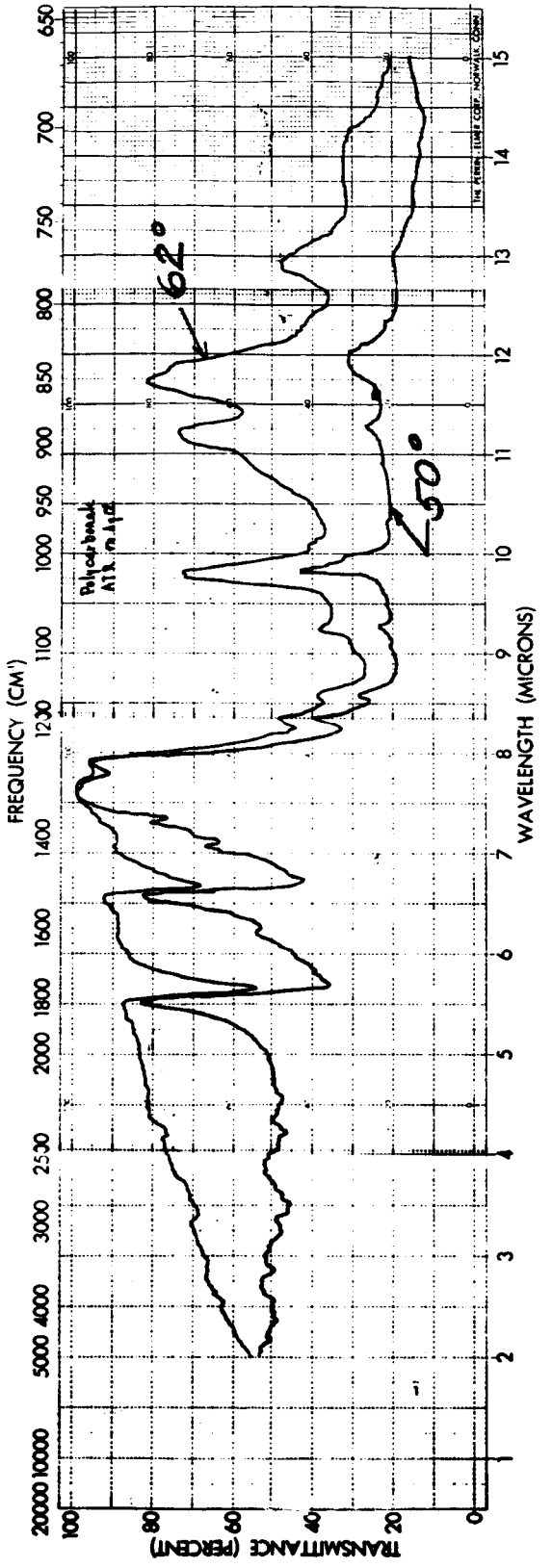

Figure 4

ATTENUATED TOTAL REFLECTANCE SPECTRUM
OF POLYCARBONATE ON SILVER CHLORIDE

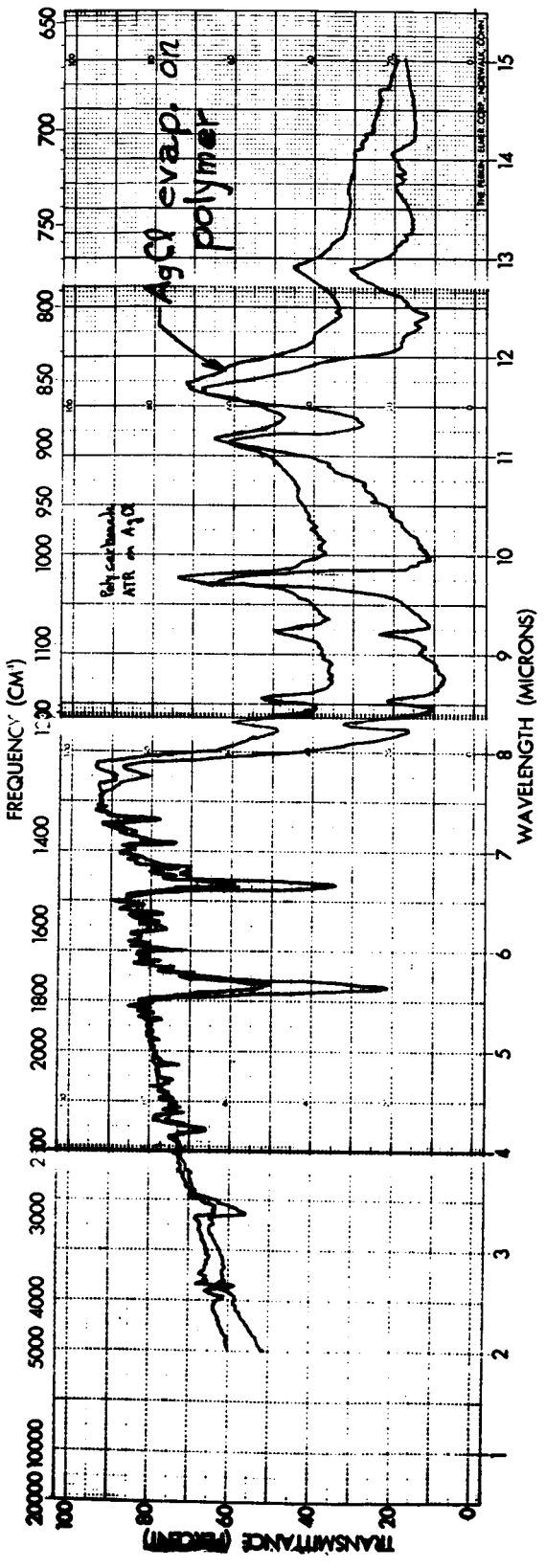

Figure 5
ATTENUATED TOTAL REFLECTANCE SPECTRUM
OF POLYCARBONATE ON SILVER CHLORIDE AT 61°C

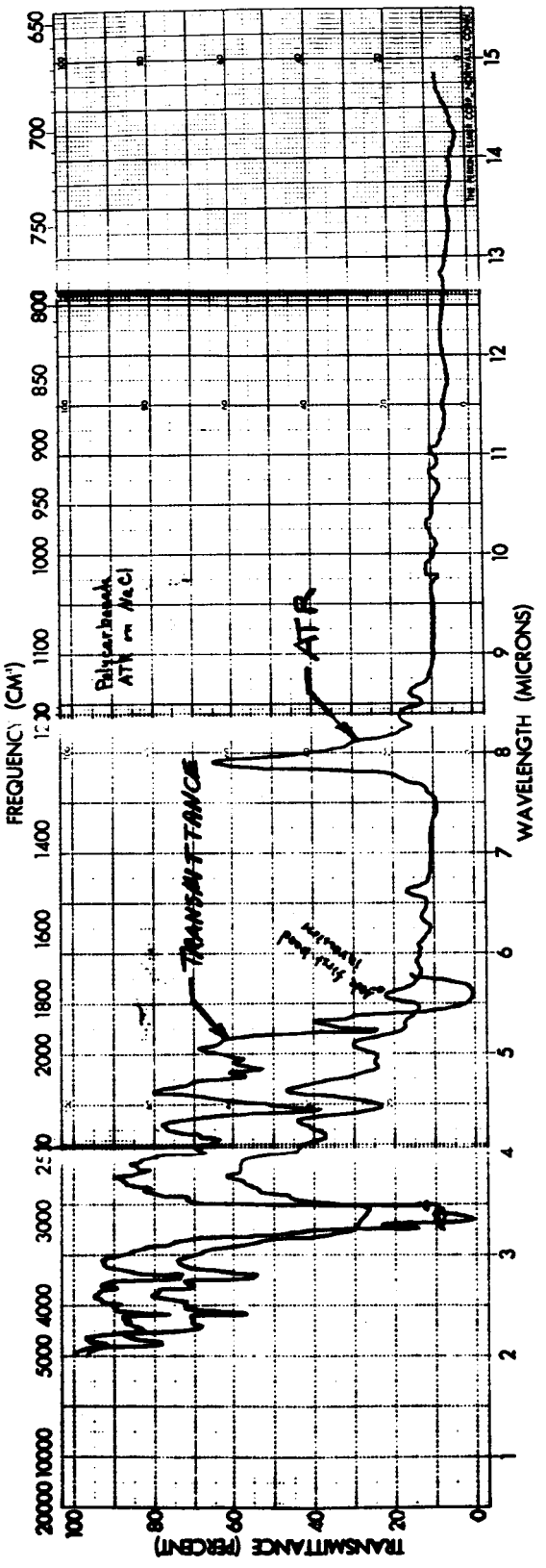

Figure 6

COMPARISON OF TRANSMITTANCE AND ATTENUATED TOTAL REFLECTANCE SPECTRA OF POLYCARBONATE
(ATR Against Sodium Chloride at 59°C)

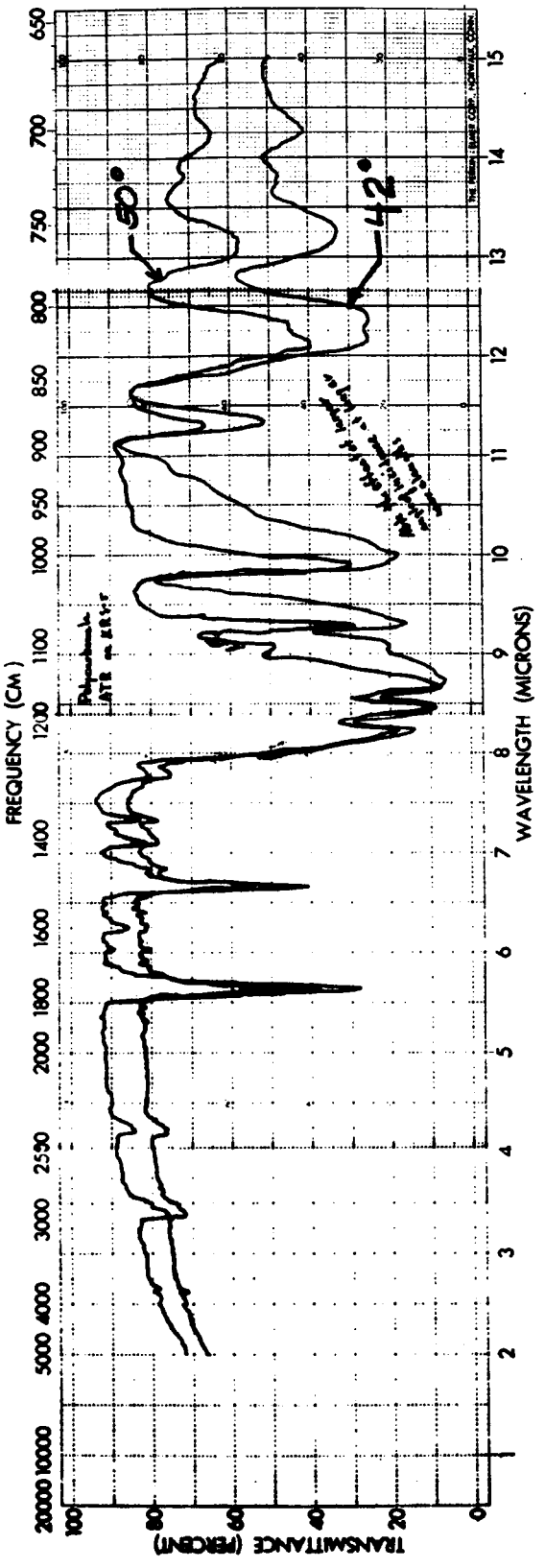

Figure 7

ATTENUATED TOTAL REFLECTANCE SPECTRUM
OF POLYCARBONATE ON KRS-5

VI. CONCLUSIONS

1. Aging of silicate paints for up to 8 months appears to cause moderate degradation when irradiated with ultraviolet in vacuum. Wrapping in Saran for long periods of time does not appear adequate to retain stability.

2. Recent tests have shown the clear superiority of zinc oxide over tin oxide and calcined china clay for use in an ultraviolet/vacuum environment.

3. Diethylenetriamine (DETA) can be used to provide room temperature-curing of methyl silicone coatings. DETA-cured paints, particularly LTV-602 coatings, are sensitive to the amount of catalyst. DETA-cured resin paints are very brittle and fail catastrophically when heated and cooled or when immersed in liquid nitrogen.

4. A zinc oxide paint based upon a recently synthesized distilled methyl silicone resin exhibited exceptional stability to ultraviolet in vacuum after being soiled and cleaned with Alconox and water.

5. A careful experiment designed to determine the extent of bleaching, if any, exhibited by zinc oxide paints showed that no more than 1% reflectance changes occur when irradiated specimens are admitted to air.

6. Recent work with attenuated total reflectance has shown that this analytical technique might be ideally suited to the problem of determining the changes in structure exhibited by methyl silicone and inorganic silicate paints on ultraviolet irradiation in vacuum. Some of the earlier difficulties with this technique have been overcome, and future work will involve thermal-control coatings.

APPENDIX I - COATING AND RESIN NUMBERS

No. Used in This Report	No. Used in Previous Reports
INORGANIC COATINGS	
Z97	6-5-11
Z98	5-6-3
Z99	CO_2-500
Z100	5-19-4a
Z101	5-19-4b
Z102	5-19-3
Z103	5-19-17
Z104	5-17-0
Z105	6-22-13
Z106	6-24-1
Z107	7-2-10
Z108	7-1-6
Z109	6-19-1
Z110	6-19-2
Z111	6-19-3
Z112	6-20-06
Z113	6-20-40
EXPERIMENTAL SILICONE RESINS	
R-10	S-38-8
R-11	S-38-11

APPENDIX II - ERRATA

The following errors are from the Summary Report No. 4 IITRI-C207-25, dated August 27, 1963:

p 149, para 2, line 9: "1.2×10^6" should be "1.2×10^7."

p 178, para 3, line 3: "0.21 to 0.25" should be "0.21 to 0.27."